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(54) Title: UNSATURATED POLYESTER RESIN COMPOSITIONS CONTAINING COMPATIBLE COMPOUNDS

(57) Abstract

A sheet molding composition is disclosed which includes a four component resinous system which comprises (a) an unsaturated polyester comprising a polycondensation product of one or more dihydric alcohols and one or more ethylenically unsaturated polycarboxylic acids; (b) one or more low-profile additives which are thermoplastic polymers which cause phase separation and porosity during the curing reaction; (c) one or more olefinically unsaturated monomers which copolymerize with the unsaturated polyester; and, (d) one or more compatible components comprising at least one compound containing one or more polyoxyethane substituents. The compatible components remain compatible when the polyester and monomer cure and impart improved surface characteristics when added to low-profile resin systems.

* See back of page

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DESCRIPTION

UNSATURATED POLYESTER RESIN COMPOSITIONS CONTAINING COMPATIBLE COMPOUNDS

TECHNICAL FIELD

The present invention provides unsaturated polyester resin compositions that contain one or more unsaturated polyesters, ethylenically unsaturated monomers that copolymerize with the unsaturated polymer, thermoplastic low-profile additives and compatible compounds.

Unsaturated polyester resin compositions are finding increased use in the automotive industry as sheet molding compound (SMC) formulations from which component parts especially body panels can be molded. The unsaturated polyester resin compositions contain, in addition to the unsaturated polyesters and monomer components, so-called "low-profile" additive components which are thermoplastic polymers that act to prevent undesirable shrinkage as the composition is being molded into a thermoset article. Low-profile additives are added to unsaturated polyester resin compositions in order to obtain a composition which can be used in a sheet molding formulation and molded into thermoset articles. The surfaces of the molded articles truly reflect the surface characteristics of the mold.

Two types of low-profile systems are commonly used commercially, one- pack and two-pack. In one-pack systems, the unsaturated polyester, monomer and low-profile additive components are mutually compatible, i.e., no gross separation occurs when a

mixture of the components is allowed to stand. In contrast, two-pack systems form distinct phases if the components are allowed to stand after being mixed. As such, the components need to be mixed immediately prior to use. In both systems, phenomena occur that allow these resins to microscopically compensate for shrinkage.

It is the ability of the low-profile resins to compensate for shrinkage that leads to the usefulness of these resins. This shrinkage compensation is largely a result of a micro-phase separation that occurs in these unsaturated polyester resin systems. The micro-phase separation occurs during the cure phase for both the one-pack and two-pack systems. Prior to cure the low-profile additive is at least partly soluble in the polyester/monomer solution. As the polyester/monomer mixture crosslinks, the low-profile thermoplastic additive and copolymer (of polyester and monomer) become increasingly less compatible and a two-phase (domain-matrix) type morphology results. This micro-phase separation leads to the formation of a porous structure as the opposing internal stresses of thermal expansion and polymerization shrinkage occur. In many unsaturated polyester resin compositions the porous structure is a result of microfracturing of the curing resins which gives rise to void formation. Unsaturated polyester resin compositions have been developed which have essentially zero shrinkage and which, in fact, expand upon curing.

In addition to unsaturated polyester resins, the sheet molding compound formulations typically contain other ingredients including, for example, chemical thickeners. In such formulations, a chemical thickener such as an alkaline material (for example, magnesium oxide or magnesium hydroxide) is added to an uncured polyester along with fillers, glass fiber, and other standard materials. The alkaline material interacts with the residual acidity in the polyester and, usually, the low-profile additive to increase the viscosity of the composition. This process is referred to as maturation and usually takes several days. If two-pack resin systems are used, care has to

be taken to avoid gross phase separation. After the maturation process is complete, the thickened formulations are handlable and can easily be placed into compression molds either by hand or by machine.

Although the use of low-profile additives does effect some degree of improvement in the anti-shrinkage characteristics of the unsaturated polyester compositions, it has now been found that significant improvements in surface smoothness and processing characteristics can be achieved by adding a component which remains compatible during the curing of the unsaturated polyester and monomer.

BACKGROUND ART

Low-profile resins have been described that contain unsaturated polyester resins, thermoplastic low-profile additives, and a polymerizable monomer, usually styrene. In addition to these components other materials have been added to low-profile systems to improve specific properties.

The Iseler, et al. Patent No. 4,622,354 describes "phase stabilizing agents" that comprise a select group of compounds from three classes: fatty acids, dimer acids and polyester polyols. When used in an SMC formulation where the thermoplastic low-profile additive is polymethylmethacrylate and a urethane prepolymer is included, the phase stabilizing agent reduces the gross separation that occurs during the maturation process. The resin compositions described by Iseler et al. are two-pack systems that formerly phase-separated during maturation prior to the addition of the phase stabilizers.

The Ochsenbein et al. U.S. Patent No. 4,473,544 describes an anti-shrink additive with a tri- or tetrafunctional polyether condensation product of propylene oxide or a triol or tetrol wherein the condensation product is acidified in such a manner that it possesses at least one terminal acidic functional group per elementary molecule. This material is used as a low-profile additive.

The Atkins U.S. Patent No. 4,555,534 describes low-shrink pigmentable unsaturated polyester resins which comprises a polyester resin comprising the reaction product of an olefinically unsaturated dicarboxylic acid or anhydride and a polyol, an olefinically unsaturated monomer, a thickening agent, a pigment, a carboxylated vinyl acetate polymer low-profile additive, and a surface active compound. The Atkins '534 patent describes low-shrink resins having improved uniformity of pigmentation in internally pigmented thickened polyester molding compositions. These pigmentable resin systems are low-shrink, and not low-profile. The surface quality of these pigmentable systems is considerably inferior to surfaces required for automotive appearance applications.

Although the use of low-profile additives and thickening agents, as described, do effect some degree of improvement in the antishrinkage and surface smoothness characteristics of the unsaturated polyester compositions, it is still not possible to achieve the degree of surface smoothness required of today's thermoset molded articles.

DISCLOSURE OF INVENTION

The present invention provides low-profile resin compositions having improved surface smoothness which are useful for compression or injection molding into useful articles. In one aspect, the invention comprises an improved sheet molding composition that includes a four component resinous system comprising:

(a) an unsaturated polyester comprising a poly condensation product of one or more dihydric alcohols and one or more ethylenically unsaturated polycarboxylic acids;

(b) one or more low-profile additives comprising thermoplastic polymers which cause phase separation and porosity during the curing reaction;

(c) one or more olefinically unsaturated monomers which copolymerize with the unsaturated polyester; and,

(d) one or more components that remain compatible during the curing of the polyester and monomer cure and contain one or more polyoxyethane substituents.

The four component resinous system imparts improved surface smoothness when used with other known, conventional ingredients for low-profile resin systems used in making sheet molding compositions.

BEST MODE OF CARRYING OUT INVENTION

The present invention relates to the discovery of the use in a low-profile system of components which remain compatible with a curing unsaturated polyester resin and monomer. When these compatible components are included in combination with low-profile additives and used in sheet molding compositions, articles with very smooth surfaces may be molded. Additionally, the flow of the sheet molding composition during the molding process is improved to the point that rapidly curing formulations may be composed. As a result, the molding time is drastically reduced.

The unsaturated polyester component of the four component resinous system comprises the polycondensation reaction product of one or more dihydric alcohols and one or more ethylenically unsaturated polycarboxylic acids. By polycarboxylic acid is generally meant the polycarboxylic or dicarboxylic acids or anhydrides, polycarboxylic or dicarboxylic acid halides, and polycarboxylic or dicarboxylic esters. Suitable unsaturated polycarboxylic acids, and the corresponding anhydrides and acid halides that contain polymerizable carbon-to-carbon double bonds may include maleic anhydride, maleic acid, and fumaric acid. A minor proportion of the unsaturated acid, up to about forty mole percent, may be replaced by dicarboxylic or polycarboxylic acid that does not contain a polymerizable carbon-to-carbon bond. Examples of which include O-phthalic, isophthalic, terephthalic, succinic, adipic, sebacic, methyl-succinic, and the like. Dihydric alcohols that are useful in preparing the polyesters include 1,2-propane diol (hereinafter referred to as

propylene glycol), dipropylene glycol, diethylene glycol, 1,3-butanediol, ethylene glycol, glycerol, and the like. Examples of suitable unsaturated polyesters are the polycondensation products of (1) propylene glycol and maleic and/or fumaric acids; (2) 1,3-butanediol and maleic and/or fumaric acids; (3) combinations of ethylene and propylene glycols (approximately 50 mole percent or less of ethylene glycol) and maleic and/or fumaric acid; (4) propylene glycol, maleic and/or fumaric acids and dicyclopentadiene reacted with water. In addition to the above described polyesters one may also use dicyclopentadiene modified unsaturated polyester resins as described in the Pratt et al. Patent No. 3,883,612. These examples are intended to be illustrative of suitable polyesters and are not intended to be all-inclusive. The acid number to which the polymerizable unsaturated polyesters are condensed is not particularly critical with respect to the ability of the low-profile resin to be cured to the desired product. Polyesters which have been condensed to acid numbers of less than 100 are generally useful, but acid numbers less than 70 are preferred. The molecular weight of the polymerizable unsaturated polyester may vary over a considerable range, but ordinarily those polyesters useful in the practice of the present invention have a molecular weight ranging from 300 to 5000, and more preferably, from about 500 to 5000.

In preferred embodiments, the unsaturated polyester is present in amounts ranging from about 20 to 45 percent, by weight, based on the total four component resinous system comprising the unsaturated polyester, the low-profile additive, monomer and compatible component. Especially preferred concentrations of the unsaturated polyester are in the 28 to 35 percent, by weight, range.

Low-profile additives are materials that when mixed in an unsaturated polyester and cured, result in a multiphase system. If the low-profile additive and the unsaturated polyester are compatible (from the standpoint that a gross phase separation does not take place) before cure, the system is known as a one-pack. Those

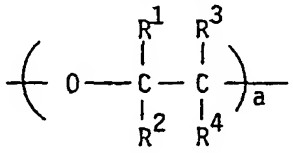
mixtures which tend to separate into two or more layers on standing are known as a two-pack resin systems. This does, however, necessitate mixing immediately before use. Some polymers that are useful as low-profile additives include homopolymers and copolymers of acrylic and methacrylic acid esters, cellulose acetate butyrate, vinyl acetate homopolymers and copolymers, polyurethanes prepared from polyisocyanates, preferably diisocyanates, and polyether polyols, numerous saturated polyesters, polycaprolactone, styrene-butadiene copolymers, some modified celluloses, and certain alkyl oxide polymers. The above list of low-profile additives is not intended to list all low-profile additives but rather to show examples of materials which have been used to cause the multiphase morphology present in low profile resins. In preferred embodiments the thermoplastic additive is present in amounts ranging from 5 to 30 percent, by weight, based on the total four component resinous system. Especially preferred concentrations of thermoplastic additive are in the 7 to 20 percent, by weight range.

The monomer component of the resinous system comprises materials that copolymerize with the unsaturated polyester. The olefinically unsaturated monomer that is copolymerizible with the unsaturated polyester is most generally styrene, however, methyl-styrene is also useful. In preferred embodiments the monomer is present in amounts ranging from 25 to 65 percent, by weight, based on the total four component resinous system. Especially preferred concentrations of monomer are in the 35 to 50 percent, by weight range.

In the present invention one or more components are added which are compatible with the unsaturated polyester and monomer during the cure phase. That is, they do not act as low-profile additives. They do not cause a microphase separation during cure. According to the present invention, these compatible components give the added benefits of surface smoothness and better flowability, when compared with low-profile resin compositions without the

compatible components. In the preferred embodiments the compatible component is present in amounts ranging from 0.5 to 15 percent, by weight, based on the total four component resinous sytem. Especially preferred concentrations of the compatible components are in the 1 to 8 percent, by weight range.

The compatible components of the present invention contain one or more oxyethane units, i.e.,



I

wherein R^1, R^2, R^3, and R^4, are selected from the group consisting of hydrogen, cycloalkyl, lower alkyl, phenyl, phenyl substituted by halogen, lower alkyl, acyl, or lower alkoxy; and phenyl lower alkyl wherein phenyl may be substituted by halogen, lower alkyl or lower alkoxy; R^1, R^2, R^3, and R^4, may be the same or different; and a is an integer between about 1 and 200, and in some embodiments a is less than 100 and in certain embodiment a is between 3 and 70.

The following terms used herein: "cycloalkyl", "lower alkyl", "lower alkoxy", "lower phenyl" and "acyl" generally contain from 1 to 50 carbons, as is well understood by those skilled in the art.

One example of a compatible component is a compound containing one or more polyoxyethane substituents for the Formula I above wherein R^1, R^2, R^3 and R^4 are selected from the group consisting of H and lower alkyl; R^1, R^2, R^3 and R^4 may be the same or different; and, a is an integer between 1 and about 200, and in certain embodiments between 1 and about 70. Another example of a compatible component is wherein $R^1 = R^2 = R^3 = R^4 = H$, and a is an integer between 1 and 200, and in certain embodiments between 1 and about 70. Another example wherein R^1 or R^2 or R^3 or $R^4 = CH_3$, and the others = H, and a is an integer between 1 and 200, and in certain embodiments between 1 and about 70.

It is desirable that the molecular weight of the compatible component is less than about 4000, the weight percent of the

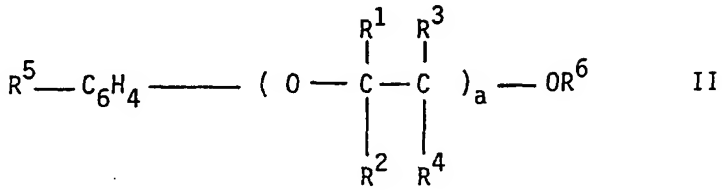
oxyethane unit described above is greater than or equal to 20, and the other atoms total is less than 240. In certain embodiments the compatible component wherein the molecular weight is less than about 3000; the weight percent of the oxyethane unit described above is greater than or equal to 20, and the other atoms total is less than about 200.

The molecular weight of the compatible compound is such that the compatible component remains compatible with the curing unsaturated polyester and monomer. Compatibility generally means that the combination of unsaturated polyester and low-profile additive do not cause the microporous phase separation widely accepted as necessary for the low-profile phenomenon. Low-profile additive components, by definition, are incompatible with the curing unsaturated polyester and monomer, and cause phase separation.

One example of compatible components that contain polyoxyethane substituents are polymers such as a polyalkylene oxide which has a molecular weight of between about 200-5000. The molecular weight of the polyalkylene oxide polymer is such that the compatible component remains compatible with the curing unsaturated polyester and monomer. When the molecular weight of the polymer is too high, the polyalkylene oxide polymer is incompatible with the curing unsaturated polyester and monomer. At that point the polyalkylene oxide polymer acts like a low-profile additive component, which, by definition, is incompatible with the curing unsaturated polyester and monomer. Specific examples of polyalkylene oxide polymers useful as compatible components include polypropylene oxide having a molecular weight between about 200-1000 and polyethylene oxide having a molecular weight between about 200-5000.

Other examples of compatible components containing one or more polyoxyethane substituents are polyalkoxylated alkyl phenols such as polypropoxylated nonyl phenols, polyethoxylated nonyl phenols, polypropoxylated octyl phenols, polyethoxyated octyl

phenols, and the like. Structure II below is an example of a polyalkoxylated alkyl phenol:

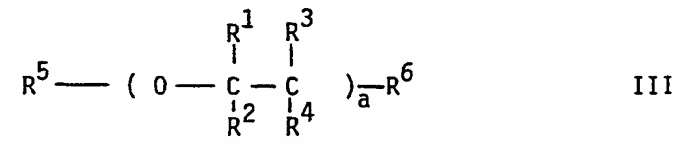


II

wherein R^1, R^2, R^3, R^4 R^5 and R^6 are selected from the group consisting of hydrogen, cycloalkyl, lower alkyl, phenyl, phenyl substituted by halogen, lower alkyl, acyl, or lower alkoxy; phenyl lower alkyl wherein phenyl may be substituted by halogen, lower alkyl or lower alkoxy; R^1, R^2, R^3, R^4, R^5 and R^6 may be the same or different; and a is an integer between 1 and about 200.

Specific examples of alkoxylated alkyl phenols include wherein a = 8-10, $R^1=R^2=R^3=R^4=$ H, $R^5 = C_8H_{17}$ and R^6=H; and wherein a = 8-10, and R^1 or R^2 or R^3 or $R^4 = CH_3$ and the others = H, $R^5 = C_8H_{17}$ and R^6 = H.

The following examples also illustrate that this oxyethane unit may be attached to numerous types of structures and be effective. An example of a compound that contains one of these oxyethane units is shown:



III

wherein R^1, R^2, R^3, R^4 are selected from the group consisting of hydrogen, cycloalkyl, lower alkyl, phenyl, phenyl substituted by halogen, lower alkyl, acyl, or lower alkoxy; R^5, and R^6 are selected from the group consisting of hydrogen, substituted benzyl, cycloalkyl, lower alkyl, phenyl, phenyl substituted by halogen, lower alkyl, acyl, or lower alkoxy, R^1, R^2, R^3, R^4, R^5 and R^6 maybe the same or different, and a is an integer between 1 and about 200.

Specific examples include:

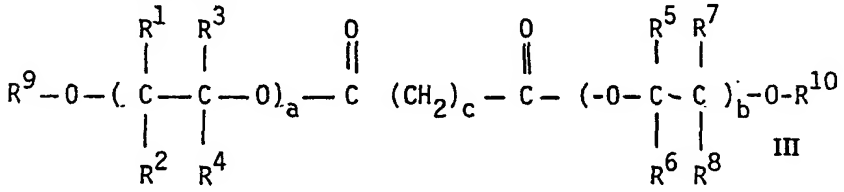
Wherein R^1 or R^2 or R^3 or R^4 = CH_3 and the others = H, R^5 = CH_3, and R^6 is $OCOCH_3$, a=2. This is dipropylene glycol monomethyl ether acetate.

Wherein R^1 or R^2 or R^3 or R^4 = CH_3 and the other = H, R^5 = CH_3, and R^6 is OH, a=2. This is dipropylene glycol monomethyl ether.

Wherein R^1 or R^2 or R^3 or R^4 = CH_3 and the other = H, R^5 = CH_3, and R^6 is OH, a=3. This is tripropylene glycol monomethyl ether.

Wherein R^1, R^2, R^3, and R^4 = H, R^5 = CH_3, and R^6 = OH, a=2. This is diethylene glycol monomethyl ether.

Still other examples of compatible components containing one or more polyoxyethane substituents are esters of polyfunctional acids where the alcohols are polyalkylene oxide monoalkyl ethers. The structures below are illustrative:



III

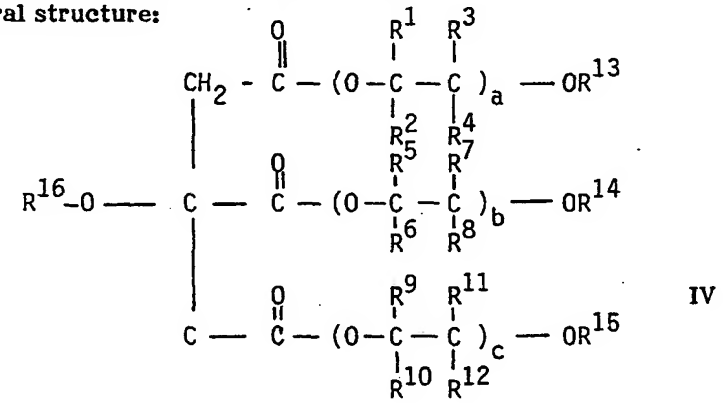
wherein R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9 and R^{10} are selected from the group consisting of hydrogen, cycloalkyl, lower alkyl, phenyl, phenyl substituted by halogen, lower alkyl, acyl, or lower alkoxy and phenyl lower alkyl wherein phenyl may be substituted by halogen, lower alkyl or lower alkoxy, and R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9 and R^{10} may be the same or different; a and b are integers

between 1 and about 200 and a and b may be the same or different, and c is an integer between 1 and about 30 and may be the same or different than a or b.

Specific examples of these compatible components include, for example, esters of citric acid, adipic acid and/or sebacic acid with tripropylene glycol monomethyl ether, dipropylene glycol monomethylether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether and the like.

Specific examples of esters of polyfunctional acids include wherein a=3, $R^1 = R^2 = R^3 = R^4 = H$, b = 3, $R^5 = R^6 = R^7 = R^8 = H$, c = 4, $R^9 = R^{10} = CH_3$; and wherein a = 3, R^1 or R^2 or R^3 or $R^4 = CH_3$ and the others = H, b = 3, R^5 or R^6 or R^7 or $R^8 = CH_3$ and the others = H, c = 4, $R^9 = R^{10} = CH_3$.

Still more specific examples of esters include triesters of a general structure:



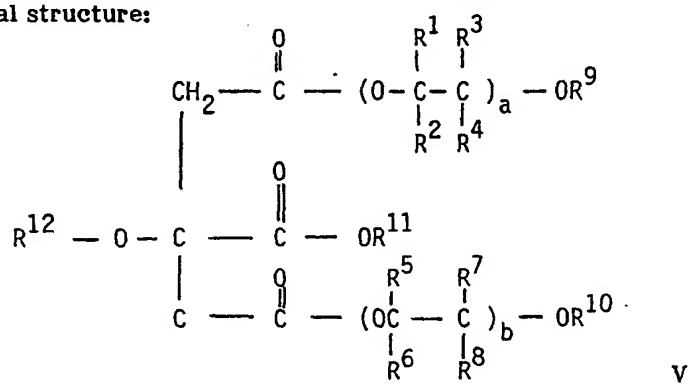
IV

wherein R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15} and R^{16} are selected from the group consisting of hydrogen, cycloalkyl, lower alkyl, phenyl, phenyl substituted by halogen, lower alkyl, acyl, or lower alkoxy and phenyl lower alkyl wherein phenyl may be substituted by halogen, lower alkyl or lower alkoxy, and R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13},

R^{14}, R^{15} and R^{16} may be the same or different, a, b, and c are integers between 1 and about 200, and a, b and c may be the same or different.

Specific examples of such triesters include wherein a = b = c = 3, $R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = R^7 = R^8 = R^9 = R^{10} = R^{11} = R^{12} =$ H, $R^{13} = R^{14} = R^{15} = CH_3$, and R^{16} = H; and wherein a = b = c = 3, R^1 or R^2 or R^3 or $R^4 = CH_3$ and the others = H, R^5 or R^6 or R^7 or $R^8 = CH_3$ and the others = H, R^9 or R^{10} or R^{11} or $R^{12} = CH_3$ and the others = H, $R^{13} = R^{14} = R^{15} = CH_3$ and R^{16} = H.

Still more specific examples of esters include diesters of a general structure:



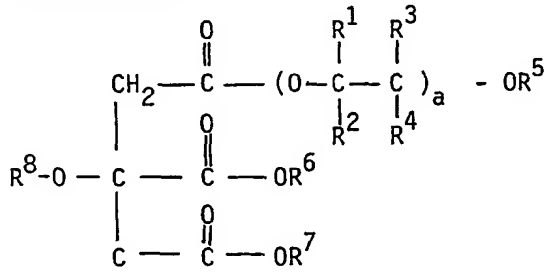
V

wherein R^1, R^2, R^3, R^4 R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11} and R^{12} are selected from the group consisting of hydrogen, cycloalkyl, lower alkyl, phenyl, phenyl substituted by halogen, lower alkyl, acyl, or lower alkoxy and phenyl lower alkyl wherein phenyl may be substituted by halogen, lower alkyl or lower alkoxy, and R^1, R^2, R^3, R^4,R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11} and R^{12} may be the same or different, a and b are integers between 1 and about 200 and b may be the same or different.

Specific examples of such diesters include wherein a = b = 3, $R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = R^7 = R^8$ = H, $R^9 = R^{10} = CH_3$ and $R^{11} =$

R^{12} = H; and wherein a = b = 3, R^1 or R^2 or R^3 or R^4 = CH_3 and the others = H, R^5 or R^6 or R^7 or R^8 = CH_3 and the others = H, R^9 = R^{10} = CH_3 and R^4 = R^{12} = H.

Still more specific examples of esters include monoesters of a general structure:



VI

R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 are selected from the group consisting of hydrogen, cycloalkyl, lower alkyl, phenyl, phenyl substituted by halogen, lower alkyl, acyl, or lower alkoxy and phenyl lower alkyl wherein phenyl may be substituted by halogen, lower alkyl or lower alkoxy, and R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 may be the same or different, and a is an integer between 1 and about 200.

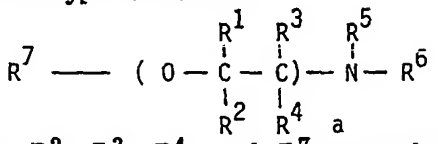
Specific examples of such monoesters include wherein a = 3, R^1 = R^2 = R^3 = R^4 = H, R^5 = CH_3 and R^6 = R^7 = R^8 = H; and wherein a = 3, R^1 or R^2 or R^3 or R^4 = CH_3 and the others = H, R^5 = CH_3 and R^6 = R^7 = R^8 = H.

In addition, the compatible components of the present invention include ethoxylated amines, such as for example,

VII-A, VII-B, VII-C

or mixtures of these wherein Z is the oxyethane unit, formula I above, R^7 and R^8 are hydrogen or a moiety containing between one and 25 carbon atoms, which may contain oxygen atoms, nitrogen atoms.

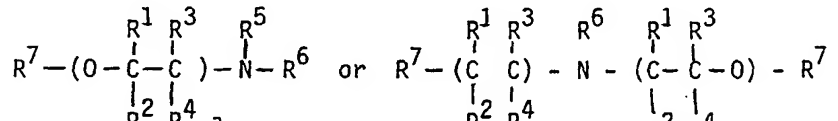
A specific type of amine is



VII

wherein R^1, R^2, R^3, R^4, and R^7 are selected from the group consisting of hydrogen, cycloalkyl, lower alkyl, phenyl, phenyl substituted by halogen, lower alkyl, acyl, or lower alkoxy, R^5, and R^6 are selected from the group consisting of hydrogen, or hydrocarbon chains containing 8-22 carbons, or cycloalkyl, lower alkyl phenyl, phenyl substituted by halogen, lower alkyl, acyl, or lower alkoxy, and a is an integer between 1 and about 200, and R^1, R^2, R^3, and R^7, may be the same or different, and R^5, and R^6, may be the same or different.

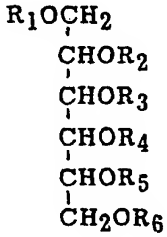
Specific examples of ethoxylated amines are Figures VIA and VIB below:



IXA, IXB

Wherein $R^1 = R^2 = R^3 = R^4 = R^5 = R^7 = H$, R^6 = hydrocarbon chains containing 8-22 carbons.

Further, the compatible components of the present invention include monosaccharides that are partially esterifed with carboxylic acid, and one or more of the remaining hydroxyls are ethoylated. For example:



X

wherein one or more of R_1, R_2, R_3, R_4, R_5, and R_6 must comprise the oxyethane group depicted in Formula I and the remainder must comprise hydrogen or $-\overset{O}{\overset{\|}{C}}-R_7$ (wherein R_7 is cycloalkyl, alkyl up to 22 carbons, lower alkyl, phenyl, phenyl substituted by halogen, lower alkyl, or phenyl).

One example of such a monosaccharide comprises an ethoxylated sorbitan monooleate with about 5 ethylene oxide units.

An additional example is an ethoxylated sorbitan monooleate with about 20 ethylene oxide units.

Other examples that illustrate the applicability of this invention are listed in Table 1 below. These additives contain one or more polyoxyethane substituents as defined in Formula I.

The four component resinous system of this invention is suitable for mixing with other ingredients in order to form a sheet molding composition. For example, the four component resinous system is suitable for mixing with chemical thickeners which are physically mixed into the resin emulsion. The chemical thickeners generally include metal oxides, hydroxides and alkoxides of Group II, III or IV from the Periodic Table. Calcium oxide and magnesium oxide or the respective hydroxides are most often employed with four component resin compositions of the present invention. In preferred embodiments, the thickener is present in amounts ranging from about 0.5 to about 6 parts, by weight, based on the four component resinous system. The thickener is generally suspended in a carrier resin, as is known in the art. In preferred embodiments the carrier material comprises a composition which does not react with the thickener such as, for example, polymethylmethacrylate, polyvinylacetate, saturated or unsaturated polyesters, and similar materials well-known in the art. In preferred embodiments the carrier resin is present in amounts ranging from about 0.5 to about 8 parts, by weight, based on one hundred parts of the four component resinous system.

Table II illustrates the preferred ranges for the four component mixture described in this invention.

Catalysts are incorporated in small amounts into thermosetting polyester resins containing ethylenically unsaturated monomer to aid in curing or cross-linking the unsaturated polyester with the monomer. Such catalysts are well known and may be similarly utilized in this invention to aid in curing the unsaturated polyester and monomer mixed with the low-profile thermoplastic polymer. Typical catalysts, for example, include organic peroxides and peracids such as tertiary butyl perbenzoate, tertiary butyl peroctoate, benzoyl peroxide and the like. The amounts of catalysts may be varied with the molding process and similarly varied with the level and types of inhibitors utilized, in a manner well known in the art. In preferred embodiments the catalyst is present in amounts ranging from about 0.5 to about 2.5 parts, by weight, based on one hundred parts of the four component resinous system.

Curing of the composition is carried out under heat and pressure typically, in closed, preferably positive pressure type molds. Mold release agents may be added to the compositions to perform their normal function, as is well understood in the art. In preferred embodiments, the mold release agents are present in amounts ranging from about 0.5 to about 6.0 parts, by weight, based on one hundred parts of the four component resinous system.

Fibers, fillers and pigments normally added to resin compositions can be likewise used in formulating the sheet molding composition of this invention. Reinforcing fibers or fibrous reinforcement is taken to mean glass fibers in one form or another, such as glass fabrics, chopped glass strands, chopped or continuous strand glass fiber mat; however, the terms also include reinforcing agents which may also be used if desired, for example, asbestos, cotton, synthetic organic fibers and metals. Fillers, usually inert, and inorganic material useful with the compositions of the present invention include, for example, clay, talc, calcium carbonate, silica, calcium silicate, and the like. In preferred embodiments the fillers are present in amounts ranging from about 165 to about 250 parts, by

weight, based on one hundred parts of the four component resinous system.

Examples of pigments include carbon black, iron oxide, titanium dioxide, and the like, as well as organic pigments. In preferred embodiments the pigments are present in amounts ranging from about 0 to about 4 parts, by weight, based on one hundred parts of the four component resinous system.

In one aspect of the present invention the preparation of the sheet molding composition is generally carried out by blending together a first portion comprising the unsaturated polyester, the low-profile additive, the monomer, the compatible component, and such additives as a catalyst, mold release agent and fillers. This is generally known in the industry as the A-side formulation. The second portion (generally known as the B-side formulation) comprises the thickening agent and a carrier resin therefor, and such additives as pigments and mold release agents. In another aspect of the invention an additional or secondary monomer is added to the B-side formulation in which the thickener is suspended. In preferred embodiments the additional monomer comprises vinyl toluene or styrene. In preferred embodiments, the additional monomer is present in amounts ranging from about 1 to about 8 parts, by weight, based on one hundred parts of the four component resinous system.

The sheet molding composition of the present invention can be prepared by mixing the components in a suitable apparatus at temperatures which are conventional and known to those skilled in the art. Once the sheet molding composition is formulated, the composition can be molded into thermoset articles having a desired shape. The actual molding cycle will, of course, depend upon the exact composition being molded. In preferred embodiments suitable molding cycles are conducted at temperatures ranging from about 121.1° - 176.7°C for periods of time ranging from about 1/3 to about 5 minutes.

INDUSTRIAL APPLICABILITY

The following formulations are provided to illustrate examples of the compositions of the present invention and are not intended to restrict the scope thereof. All parts are parts by weight, unless otherwise expressly specified.

TABLE II - Resin Compositions

Ingredients	Range (wt.%)	Range (wt.%)	Preferred
Unsaturated polyester	20-45		28-35
Thermoplastic additive (low-profile)	5-30		7-20
Monomer	25-65		35-50
Compatible component	0.5-15		1-8
	100		100

TABLE III - Sheet Molding Composition Formulations

	Formulations				
Ingredients	A	B	C	D	E
Resin	100	100	100	100	100
Catalyst	1.5	1.5	1.5	1.5	1.5
Release agent	5.0	4.5	4.5	4.5	3.5
Filler	230	220	230	180	200
Thickener	4.0	5.0	4.0	4.0	4.0
Pigment	0.1	0.2	0.1	0.1	0.1
Carrier	1.55	—	1.55	1.55	1.55
Secondary monomer	5.6	—	5.6	5.6	5.6

The sheet molding compositions of the above formulations in Table III have shown unexpected improvements in surface aesthetics and mold fillout. These improvements are especially significant for

use in sheet molding compound (SMC). Moreover, increasingly thinner automobile parts are able to be molded with smoother surfaces than by any known systems.

For formulation A the unsaturated polyester comprises maleic anhydride and propylene glycol; the low-profile additive comprises a saturated polyester made from ethylene glycol and propylene glycol and adipic acid; the monomer comprises styrene; the compatible component comprises a polypropylene oxide having a molecule weight between about 200 and 2000; the catalyst comprises tertiary butyl perbenzoate; added to the A-side, the release agent comprises calcium stearate and zinc stearate; the filler comprises calcium carbonate; the thickener comprises magnesium hydroxide; the carrier comprises polymethylmethacrylate; the pigment comprises a carbon black pigment suspension; and the secondary monomer comprises vinyl toluene.

Compression molded panels made with Formulation A with 27 percent, by weight, of 2.54 cm chopped glass fibers. When measured on a surface smoothness index instrument (LORIA® registered trademark of the Ashland Chemical Co.) the panels gave a number of 60-70 as compared to the same formulation but without the compatible component which gave a number of 80-90. On the LORIA® instrument, the lower the number, the smoother the surface.

For formulation B the unsaturated polyester comprises maleic anhydride and propylene glycol; the low-profile additive comprises a saturated polyester made from ethylene glycol and propylene glycol and adipic acid; the monomer comprises styrene; the compatible component comprises a triester of citric acid with tripropylene glycol monomethyl ether; the catalyst comprises tertiary butyl perbenzoate; the release agent comprises calcium stearate; the filler comprises calcium carbonate; the thickener comprises magnesium hydroxide; and, the pigment comprises a carbon black pigment suspension.

Compression molded panels made with Formulation B with 27 percent, by weight, of 2.54 cm chopped glass fibers. When measured on a surface smoothness index instrument (LORIA®) the panels gave a number of 55-60 as compared to the same formulation but without the compatible component which gave a number of 80-90.

For formulation C the unsaturated polyester comprises maleic anhydride and propylene glycol; the low-profile additive comprises a saturated polyester made from ethylene glycol and propylene glycol and adipic acid; the monomer comprises styrene; the compatible component comprises octyl phenol reacted with ethylene oxide where the repeating ethylene oxide units are 9-12; the catalyst comprises tertiary butyl perbenzoate; the release agent comprises calcium stearate and zinc stearate; the filler comprises calcium carbonate; the thickener comprises magnesium hydroxide suspended in a carrier comprising polymethylmethacrylate; the pigment comprises a carbon black pigment suspension; and the secondary monomer comprises vinyl toluene.

Compression molded panels made with Formulation C with 27 percent, by weight, of 2.54 cm chopped glass fibers. When measured on a surface smoothness index instrument (LORIA®) the panels gave a number of 50-60 as compared to the same formulation but without the compatible component which gave a number of 80-90.

For formulation D the unsaturated polyester comprises maleic anhydride, propylene glycol, and dicyclopentadiene; the low-profile additive comprises an acid functional copolymer of vinyl acetate and methyl methylacrylate; the monomer comprises styrene; the compatible component comprises polypropylene oxide having a molecular weight between about 200 and 2000; the catalyst comprises tertiary butyl perbenzoate; the release agent comprises zinc stearate; the filler comprises calcium carbonate; the thickener comprises magnesium hydroxide; the carrier comprises polymethylmethacrylate; the pigment comprises a carbon black pigment suspension; and the secondary monomer comprises vinyl toluene.

Compression molded panels were made with formulation D with 27 percent, by weight, of 2.54 cm chopped glass fibers. When measured on a surface smoothness index instrument, LORIA®, the panels gave a number of 152 as compared to the same formulation without the compatible component which gave a number of 175.

For formulation E the unsaturated polyester comprises maleic anhydride and propylene glycol; the low-profile additive comprises polyvinylacetate; the monomer comprises styrene; the compatible component comprises polypropylene oxide having a molecular weight between about 200 and 2000; the catalyst comprises tertiary butyl perbenzoate; the release agent comprises zinc stearate; the filler comprises calcium carbonate; the thickener comprises magnesium hydroxide; the carrier comprises polymethylmethacrylate; the pigment comprises a carbon black pigment suspension; and the secondary monomer comprises vinyl toluene.

Compression molded panels were made with formulation E with 27 percent, by weight, of 2.54 cm chopped glass fibers. When measured on a surface smoothness index instrument, LORIA®, the panels gave a number of 60 as compared to the same formulation without the compatible component which gave a number of 66.

In addition, various other formulations, using the sheet molding composition formulation shown in Table IV below, were made.

TABLE IV - Typical Sheet Molding Composition Formulation

Ingredients	Amount
Resin	100
Catalyst	1.4
Release agent	4.2
Filler	215
Thickener	3.7
Pigment	0.2
Carrier	1.9
Secondary monomer	3.7

In addition, the remaining ingredients were the same for each formulation: the unsaturated polyester comprises maleic anhydride and propylene glycol; the low-profile additive comprises a saturated polyester made from ethylene glycol and propylene glycol and adipic acid; the monomer comprises styrene; the compatible components are listed in Table I; the catalyst comprises tertiary butyl perbenzoate; the release agent comprises calcium stearate and zinc stearate; the filler comprises calcium carbonate; the thickener comprises magnesium hydroxide; the carrier comprising polymethylmethacrylate; the pigment comprises a carbon black pigment suspension; and the secondary monomer comprises vinyl toluene.

Compression molded panels were made with each formulation with 27 percent, by weight, of 2.54 cm chopped glass fibers. When measured on a surface smoothness index instrument (LORIA® registered trademark of the Ashland Chemical Co.) the panels gave the LORIA® number as listed in Table I below as compared to the same formulation but without any compatible component, which gave a number of 80-90. On the LORIA® instrument, the lower the number, the smoother the surface. The additives listed in Table I below contain the oxyethylene unit, as described in this invention. It

is within the contemplated scope of the present invention that the compatible components especially useful in the four component resinous system have a surface smoothness value within the ranges set forth in Table I below. In preferred embodiments, it is contemplated that the surface smoothness values of the four component resinous systems containing compatible components, be about 50 or less, as measured using a LORIA® surface smoothness index instrument.

TABLE 1

COMPATIBLE COMPONENT	COMMON OR TRADENAME	LORIA
Polypropylene glycol ceteareth-9	Eumulgin L	61
Polyoxyethane-co-polyoxypropane amine	Genapol PN-30	57
Polyalkoxylated quaternary amine	Cirrasol G-250	56
Polyoxypropane (10) cetyl ether phosphate	Crodafog CAP	01.5
Sodium alkylaminopolyethoxyethyl sulfate	Triton OS-15	60
Polyoxyethylated (5) Oleic Acid	Emulphor VN-430	44
Polyoxyethylated (30) Caster Oil	Emulphor EL-620	41
Polyoxyethylated (20) Oleyl Alcohol	Emulphor ON-870	43.5
Ethoxylated Mono and Diglycerides	Durfax EOM K	57
Polypropoxylated (6) Phenol	POP (6) Phenol	50
Ethoxylated Aromatic Alcohol Phosphate	Mazon JMR-1	66
Ethoxylated-Propoxylated Linear Alcohol	Rexonic P-1	62
Phosphated Alkylphenol Ethoxylate	Rexophos 25/97	76
88% Dimethyl Polyethylene Glycol 12% Acetate Silicone Copolymers	DowCorning FF-400	69
88% Polyoxyethyleneglycol Silicone Copolymer 12% Allyl Alcohol Ethoxylated	DowCorning 193	42

TABLE 1 (con't)

COMPATIBLE COMPONENT	COMMON OR TRADENAME	LORIA
Aromatic Alcohol (ethoxylated) Phosphate	Maphos JM-71	80
Ethoxylated Linear Alcohol (40% E.O.)	Alfonic 1012-40	49
Polyethoxylated (20) Glyceryl Stearate	Aldosperse MS-20-FG	42
Polyethoxylated (10) Cetyl Ether	BRIJ 56	48
Ethoxylated (20) Methyl Glucoside Sesquisterate	Glucamate SSE-20	45
Carboxylated Ethoxylated Alcohol	Emcol CBA-60	53
Polyethoxylated Lauramide MEA	Mazamide 1,-5	42
Ethoxylated Hydrogenated Lanolin	Lipolan 31	50
Propylene Glycol Stearate	Lipo PGMS	60
Alcohols (C-10 to C-16) Ethoxylated	AE-3	44
Alcohols (C-10 to C-16) Ethoxylated	AE-7	46
Carboxylated Ethoxylated Alcohol	Emcol CBA-60	53
Polyethoxylated (20) Oleyl Alcohol	ON870	44
Propylene Glycol Hydroxy Stearate	Naturechem PGHS	53
EO/PO Type Surfactant	Pluronic L-35	52
EO/PO Surfactant	Pluronic L-64	58.2
EO Adducts of Polypropylene Triols (25% polymer-30/70 Acrylonitrile-Styrene)	Union Carbide E-564	77

TABLE 1 (con't)

COMPATIBLE COMPONENT	COMMON OR TRADENAME	LORIA
Polyalkyleneoxidemethylsiloxane Copolymer	Union Carbide L-562	50
Polyethoxylated (6) Bisphenol A	POE 6 Bisphenol A	58
Polypropoxylated (6) 2-Ethylhexanol	POP 6 -2 Ethylhexanol	54
Polypropoxylated (6) Nonylphenol	POP 6 Nonylphenol	55
EO/PO Surfactant	Pluronic L-63	61
Polyoxyethylene (5) Sorbitan Monooleate	Glycosperse 0-5	56
Polyethoxylated (20) Sorbitan Monooleate	Flo Mo SMO-20	58
Polyethylene Glycol M.W. 600	Polyethyleneglycol MW 600	47
Polyethylene Glycol Monomethylether	PEGME	53
Polyethoxylated (5) Tallow Amine	TAM-5	58
Polyethoxylated (20) Sorbitan Monooleate	Tween 80	56.2
Polyethoxylated (5) Sorbitan Monooleate	Tween 81	55
Nonylphenoxy Polyethoxy Ethanol	Triton N-57	52.9
Octylphenoxy Polyethoxy Ethanol	Triton X-15	53.8
Polyoxyethylated (8) Monostearate	Ethox MA-0	45
Polyoxyethylated (9) Tallate	Ethox TO-9A	45
Polyoxyethylene Decyl Phosphate Potassium Salt	Ethfac 361	61
Polyethoxylated (5) Laurate	Ethox ML-5	45

Table 1 (con't)

COMPATIBLE COMPONENT	COMMON OR TRADENAME	LORIA
Polyethoxylated (9) Laurate	Ethox ML-9	45
Polyethoxylated (14) Laurate	Ethox ML-14	46
Polyethoxylated (9) Isostearate	Ethox MI-9	51
Polyethoxyalted (14) Isostearate	Ethox MI-14	48
Polyethoxylated (9) Oleate	Ethox MO-9	51
Polyethoxylated (14) Oleate	Ethox MO-14	44
Polyethoxylated Nonylphenol	Gedepal CO 210	59
Polyethoxylated Nonylphenol	Alaksurf NP-15	47
Ethoxylated Octyl Phenol	Triton X-45	59
Ethoxylated Octyl Phenol	Triton X-102	53
Polyoxyethane (15) Cocoamine	CAM-15	54
Dipropyleneglycol Monomethylether	DPGMME	50

In addition, the sheet molding compositions of the above formulations have shown unexpected improvements in surface aesthetics and mold fillout. These improvements are especially significant for use in sheet molding compound (SMC). Moreover, increasingly thinner automobile parts are able to be molded with smoother surfaces than by any known systems.

Although the invention has been described in its preferred form with a certain degree of particularity, it is understood that the present disclosure has been made only by way of example, and that numerous changes can be made without departing from the spirit of the scope of the invention.

CLAIMS:

1. A four component resinous system for a sheet molding composition comprising:

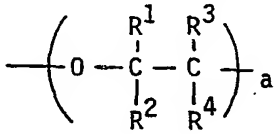
(a) an unsaturated polyester comprising a polycondensation product of one or more dihydric alcohols and one or more ethylenically unsaturated polycarboxylic acids;

(b) one or more low-profile thermoplastic polymers which cause phase separation and porosity during a curing reaction;

(c) one or more olefinically unsaturated monomers which copolymerizes with the unsaturated polyester, and,

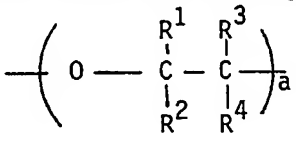
(d) one or more components which remain compatible during cure of the unsaturated polyester and monomer.

2. The composition of claim 1, wherein the compatible component is selected from the group of compounds containing one or more polyoxyethane substituents having a general structure



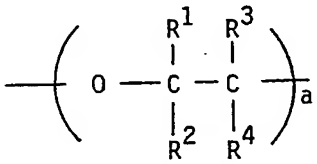
wherein R^1, R^2, R^3 and R^4 are selected from the group consisting of hydrogen, cycloalkyl, lower alkyl, phenyl, phenyl substituted by halogen, lower alkyl, acyl or lower alkoxy; phenyl lower alkyl wherein phenyl maybe substituted by halogen, lower alkyl or lower alkoxy; R^1, R^2, R^3 and R^4 may be the same or different; and a is an integer between 1 and about 200.

3. The composition of claim 1, wherein the compatible component is selected from the group of compounds containing one or more polyoxyethane substituents having a general structure:



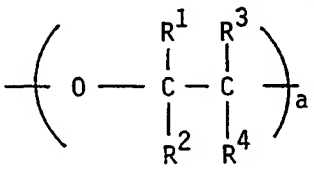
wherein R^1, R^2, R^3 and R^4 are selected from the group consisting of hydrogen or lower alkyl alkoxy; R^1, R^2, R^3 and R^4 may be the same or different; and a is an integer between 1 and about 200.

4. The composition of claim 1, wherein the compatible component is selected from the group of compounds containing one or more polyoxyethane substituents having a general structure:



wherein R^1, R^2, R^3, and R^4 = H; and a is an integer between 1 and about 200.

5. The composition of claim 1, wherein the compatible component is selected from the group of compounds containing one or more polyoxyethane substituents having a general structure:



wherein R^1 or, R^2 or, R^3 or, R^4 = CH_3 and the others = H; and a is an integer between 1 and 200.

6. The composition of claim 2, wherein the compatible component has a molecular weight less than about 4000, the weight percent of the polyoxyethane substituent is greater than or equal to 20 and other atoms in the compatible component total less than about 240.

7. The composition of claim 3, wherein the compatible component has a molecular weight less than about 4000, the weight percent of the polyoxyethane substituent is greater than or equal to 20 and other atoms in the compatible component total less than about 240.

8. The composition of claim 4, wherein the compatible component has a molecular weight less than about 4000, the weight percent of the polyoxyethane substituent is greater than or equal to 20 and other atoms in the compatible component total less than about 240.

9. The composition of claim 5, wherein the compatible component has a molecular weight less than about 4000, the weight percent of the polyoxyethane substituent is greater than or equal to 20 and other atoms in the compatible component total less than about 240.

10. The composition of claim 2, wherein the compatible component has a molecular weight less than about 3000; the weight percent of the polyoxyethane substituent is greater than or equal to 20 and the other atoms in the compatible component total less than about 200.

11. The composition of claim 3, wherein the compatible component has a molecular weight less than about 3000, the weight percent of the polyoxyethane substituent is greater than or equal to

20 and other atoms in the compatible component total less than about 200.

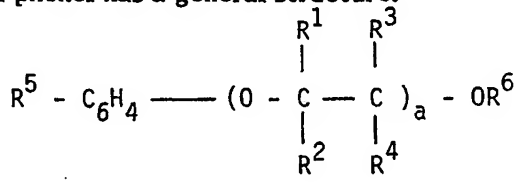
12. The composition of claim 4, wherein the compatible component has a molecular weight less than about 3000, the weight percent of the polyoxyethane substituent is greater than or equal to 20 and other atoms in the compatible component total less than about 200.

13. The composition of claim 5, wherein the compatible component has a molecular weight less than about 3000, the weight percent of the polyoxyethane substituent is greater than or equal to 20 and other atoms in the compatible component total less than about 200.

14. The composition of claim 1, wherein the compatible component has a molecular weight of between about 200-5000.

15. The compositions of claim 1, wherein the compatible component comprises one or more polyalkoxylated alkyl phenols.

16. The compositions of claim 15, wherein the polyalkoxylated alkyl phenol has a general structure:

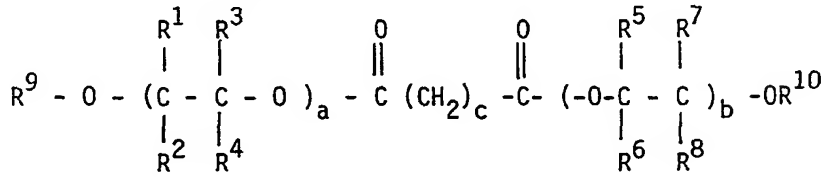


wherein R^1, R^2, R^3, R^4, R^5 and R^6 are selected from the group consisting of hydrogen, cycloalkyl, lower alkyl, phenyl, phenyl substituted by halogen, lower alkyl, acyl, or lower alkoxy and phenyl lower alkyl wherein phenyl may be substituted by halogen, lower alkyl

or lower alkoxy, R^1, R^2, R^3, R^4, R^5 and R^6 may be the same or different, and a is an integer between 1 and about 200.

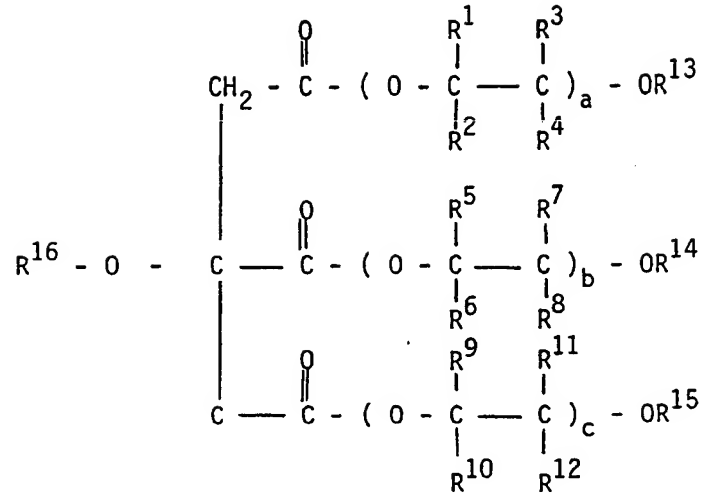
17. The compositions of claim 1, wherein the compatible component comprises one or more esters of polyfunctional acids.

18. The compositions of claim 17, wherein the esters of polyfunctional acids have a general structure:



wherein R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9 and R^{10} are selected from the group consisting of hydrogen, cycloalkyl, lower alkyl, phenyl, phenyl substituted by halogen, lower alkyl, acyl, or lower alkoxy and phenyl lower alkyl wherein phenyl may be substituted by halogen, lower alkyl or lower alkoxy, R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9 and R^{10} may be the same or different, a and b are integers between 1 and about 200, a and b may be the same or different, and c is an integer between 1 and about 30 and may be the same or different than a or b.

19. The composition of claim 17, wherein the esters are triesters having a general structure:

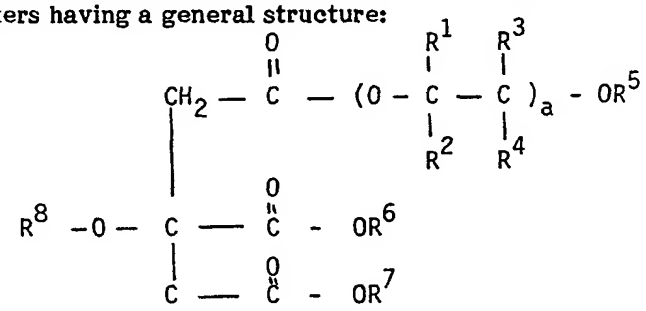


wherein R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15} and R^{16} are selected from the group consisting of hydrogen, cycloalkyl, lower alkyl, phenyl, phenyl substituted by halogen, lower alkyl, acyl, or lower alkoxy and phenyl lower alkyl wherein phenyl may be substituted by halogen, lower alkyl or lower alkoxy, and R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15} and R^{16} may be the same or different, a, b, and c are integers between 1 and about 200, and a, b and c may be the same or different.

20. The compositions of claim 17, wherein the esters are diesters having a general structure:

wherein R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11} and R^{12} are selected from the group consisting of hydrogen, cycloalkyl, lower alkyl, phenyl, phenyl substituted by halogen, lower alkyl, acyl, or lower alkoxy and phenyl lower alkyl wherein phenyl may be substituted by halogen, lower alkyl or lower alkoxy, and R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11} and R^{12} may be the same or different, a and b are integers between 1 and about 200 and a, b and c may be the same or different.

21. The compositions of claim 17, wherein the esters are monoesters having a general structure:



wherein R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 are selected from the group consisting of hydrogen, cycloalkyl, lower alkyl, phenyl, phenyl substituted by halogen, lower alkyl, acyl, or lower alkoxy and phenyl lower alkyl wherein phenyl may be substituted by halogen, lower alkyl or lower alkoxy, and R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 may be the same or different, and a is an integer between 1 and about 200.

22. The composition of claim 1, wherein the compatible component is selected from the group consisting of polyethoxylated (5) oleic acid, polyethoxylated (30) caster oil, polyethoxylated nonylphenol ether phosphate, polyethoxylated (20) oleyl alcohol, polypropoxylated (6) phenol, 88% polyoxyethyleneglycol silicone copolymer 12% allyi alcohol ethoxylated, ethoxylated linear alcohol

(40% E.O.), polyoxyethylene (20) glyceryl stearate, polyoxyethylene (10) cetyl ether, polyethoxylated (20) methyl glucoside sesquisterate, polyethoxylated (6) lauramide MEA, ethoxylated hydrogenated lanolin, alcohols (C-10 to C-16) ethoxylated, polyethoxylated (20) oleyl alcohol, polyalkyleneoxidedimethylsiloxane copolymer, polyethylene glycol M.W. 600, polyethoxylated (8) monomerate, polyethoxylated (9) tallate, polyethoxylated (5) laurate, polyethyoxlated (9) laurate, polyethoxylated (14) laurate, polyethoxylated (14) isostearate, polyethoxylated (14) oleate, polyethoxylated nonylphenol, and dipropyleneglycol monomethylether.

23. The composition of claim 1, wherein the compatible component has a surface smoothness value of about 50 or less.

24. The composition of claim 1, wherein the unsaturated polyester comprises the polycondensation product of dihydric alcohols and an ethylenically unsaturated polycarboxylic acid.

25. The composition of claim 24, wherein the unsaturated polyester is selected from the group consisting essentially of a polycondensation product of maleic and/or fumaric acids and propylene glycol; the polycondensation product of 1,3-butanediol and maleic and/or fumaric acids; the polycondensation product of ethylene and propylene glycols comprising approximately 50 mole percent or less of ethylene glycol, and maleic and/or fumaric acids; the polycondensation product of propylene glycol, maleic and/or fumaric acids and dicyclopentadiene reacted with water; and the polycondensation product of propylene glycol, maleic and/or fumaric acids and isophthalic acid.

26. The composition of claim 1, wherein the low-profile thermoplastic polymer is selected from the group consisting

essentially of a reaction product of ethylene glycol and propylene glycol and adipic acid; a polyvinyl acetate homopolymer or copolymer; and a polymethylmethacrylate.

27. The composition of claim 1, wherein the monomer is selected from the group consisting essentially of styrene, methyl-styrene, and vinyl toluene.

28. The composition of claim 1, wherein the unsaturated polyester is present in an amount of approximately 25-45 percent, the low-profile thermoplastic polymer is present in an amount of approximately 5-30 percent, the monomer is present in an amount of approximately 25-65 percent and, the compatible component is present in an amount of approximately 0.5-15 percent, by weight, of the four component resin.

29. The composition of claim 12, wherein the unsaturated polyester is present in an amount of approximately 28-35 percent, the low-profile thermoplastic polymer is present in an amount of approximately 7-20 percent, the monomer is present in an amount of approximately 35-50 percent and, the compatible component is present in an amount of approximately 1-8 percent, by weight, of the four component resin.

AMENDED CLAIMS
[received by the International Bureau
on 24 April 1991 (24.04.91);
original claim 2 cancelled;
original claim 1 amended;
other claims unchanged (1 page)]

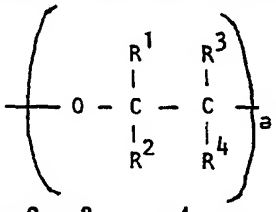
1. (AMENDED) A four component resinous system for a sheet molding composition comprising:

(a) an unsaturated polyester comprising a polycondensation product of one or more dihydric alcohols and one or more ethylenically unsaturated polycarboxylic acids;

(b) one or more low-profile thermoplastic polymers which cause phase separation and porosity during a curing reaction;

(c) one or more olefinically unsaturated monomers which copolymerizes with the unsaturated polyester, and,

(d) one or more components which remain compatible during cure of the unsaturated polyester and monomer, wherein the compatible component is selected from the group of compounds containing one or more polyoxyethane substituents having a general structure



wherein R^1, R^2, R^3 and R^4 are selected from the group consisting of hydrogen, cycloalkyl, lower alkyl, phenyl, phenyl substituted by halogen, lower alkyl, acyl or lower alkoxy; phenyl lower alkyl wherein phenyl maybe substituted by halogen, lower alkyl or lower alkoxy; R^1, R^2, R^3 and R^4 may be the same or different; and a is an integer between 1 and about 200.

2. (CANCELLED)

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 90/05541

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: C 08 L 67/06

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
IPC5	C 08 L

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category *	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	EP, A2, 0335406 (UNION CARBIDE CORPORATION) 4 October 1989, see the whole document --	1-29
X	US, A, 4622354 (ISELER ET AL) 11 November 1986, see column 4, line 21 - line 35; abstract; claims 1-54 --	1
X	US, A, 4555534 (KENNETH E. ATKINS) 26 November 1985, see column 4, line 45 - line 68; abstract --	1-5

* Special categories of cited documents:[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
21st February 1991	07 MAR 1991
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	MISS T. TAZELAAR

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	EP, A1, 0377769 (KANEGAFUCHI KAGAKU KOGYO KABUSHIKI KAISHA) 18 July 1990, see the whole document	1-29
A	EP, A1, 0304122 (STAMICARBON B.V.) 22 February 1989, see the whole document	1-29
A	US, A, 4472544 (OCHSENBEIN ET AL) 18 September 1984, see the whole document	1-29

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. PCT/US 90/05541

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 31/01/91 The European Patent office is in no way liable for theseparticulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A2- 0335406	04/10/89	JP-A-	2014239	18/01/90
US-A- 4622354	11/11/86	AU-B-	582446	23/03/89
		AU-D-	5834286	30/04/87
		CA-A-	1267988	17/04/90
		EP-A-	0222977	27/05/87
		EP-A-	0365051	25/04/90
		EP-A-	0365052	25/04/90
		JP-A-	62100537	11/05/87
US-A- 4555534	26/11/85	NONE		
EP-A1- 0377769	18/07/90	JP-A-	1020219	24/01/89
		US-A-	4943474	24/07/90
EP-A1- 0304122	22/02/89	JP-A-	1069615	15/03/89
		NL-A-	8701932	16/03/89
		US-A-	4948821	14/08/90
US-A- 4472544	18/09/84	EP-A-	0101343	22/02/84
		FR-A-B-	2531092	03/02/84
		JP-A-	59038222	02/03/84